

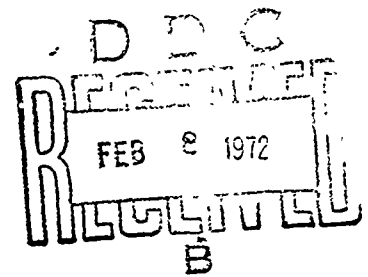
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SOLID PROPELLANT KINETICS

III. EXPERIMENTAL STUDY OF THE OPPOSED FLOW SOLID
PROPELLANT DIFFUSION FLAME* +

S. H. Inami and H. Wise
Stanford Research Institute
Menlo Park, California 94025



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ABSTRACT

The kinetics of high-temperature reactions associated with solid-propellant deflagration are studied quantitatively by means of the heterogeneous opposed flow diffusion flame. In these experiments a cylindrical gas jet containing the gaseous fuel impinges on the surface of a solid propellant composed of ammonium perchlorate (AP) and copper chromite (CC) catalyst. A diffusion flame is established in the stagnation region formed by the two opposed flows of reactants. With increasing mass flux of gaseous fuel, the mass flux of solid AP/CC grows until a limiting condition is reached governed by the kinetics of reaction. Further enhancement in fuel flow does not result in any increase in the mass consumption rate of solid oxidizer. This condition of maximum reaction rate may be used in conjunction with a theoretical analysis to evaluate the kinetics of gas-phase reaction of the propellant system. The effects of various parameters on the kinetics of reaction were examined, including the catalyst concentration in the solid phase, the fuel concentration in the gas phase, and the temperature of the gaseous fuel. For the system AP/CC/methane an activation energy of 20 Kcal/mole is evaluated for the gas phase reaction.

Introduction

Current theoretical models¹ of composite solid propellant combustion are based on an analysis of heat transfer from a two-stage flame to the solid surface undergoing sublimation.¹ The first stage of the flame is considered to be a thin, premixed exothermic reaction zone fed by ammonia and perchloric acid from the decomposition of ammonium perchlorate (AP). In the second stage, the combustion of fuel and oxidant molecules is postulated under conditions controlled by diffusional mass transport or chemical reaction rates. Although such a model does not take into account the heterogeneous reactions occurring near the subsurface of the propellant and at the solid/gas interface², especially in the presence of catalysts, it has been moderately successful in providing a semiquantitative description of the burning characteristics of propellants as a function of such variables as gas pressure and AP particle size. However, to advance and refine the theoretical model further, one needs quantitative information on the kinetics of gas-phase reactions of the propellant components at flame temperatures.

An experimental approach to this problem is the heterogeneous opposed flow diffusion flame (HOFD) fed by a solid oxidizer and a gaseous fuel. This technique is based on the earlier work done by Potter and coworkers^{3,4} who demonstrated that the extinction of a homogeneous diffusion flame formed between two opposed gaseous jets--one gaseous fuel, the other, gaseous oxidizer--is a measure of the maximum reaction rate. Also in 1961 Friedman⁵ made some preliminary measurements of the burning rate of AP onto which a jet of gaseous fuel was impinging.

A theoretical analysis^{6,7} of the homogeneous diffusion flame indicated the relationships between the mass fluxes of fuel and oxidant at extinction, the chemical kinetics of the system, and the laminar flame speed in premixed gases. In a more recent publication⁸ we have

removed the assumption made by Spalding⁶ concerning the proportionality between gas velocity and distance from the stagnation point. Also we have extended the theoretical approach to the HOFD involving a solid oxidizer and a gaseous fuel system. In contrast to the homogeneous system, the conditions prevalent at the gas/solid interface are no longer an independent variable. By means of this analysis we are able to interpret the experimental data to be presented in terms of reaction-rate kinetics.

Experimental Details

To examine at combustion temperatures the gas-phase rate processes involving fuel and the intermediate products of the catalyzed decomposition of AP, we have constructed the experimental apparatus depicted in Figure 1. In this system a cylindrical gas jet containing the fuel (methane, in the current work) is allowed to impinge on the surface of a solid propellant composed of AP and copper chromite (CC). The solid is contained in a copper block provided with a closely fitting opening through which the propellant may be advanced by means of a motor-driven mechanical piston. The top surface of the solid is perpendicular to the gas jet. The centerline of both units is coincident, but the distance between them may be adjusted.

After ignition of the propellant strand (a cylinder with a diameter of 0.6 cm) by means of an electrically heated resistance wire, a flame nearly flat in appearance is established in the stagnation region formed by the flow of gaseous fuel and decomposition products of the AP/CC. For a given mass flux of gaseous fuel the steady-state consumption rate of the solid propellant may be evaluated by matching the rate of advance of the propellant strand to its consumption rate so that the distance between gaseous fuel outlet and propellant surface remains constant. Condensation of liquid combustion products on the cool

portions of the propellant is obviated by providing the opening in the copper block, through which the solid emerges, with a small conical section (Fig. 1). The combustion products are swept away in a gas stream of the same composition as the gas in the fuel jet. This carrier stream enters the cylindrical chamber (Pyrex, 4 inches in diameter), in which the HOFD is located, through openings in the support plate located at the bottom of the apparatus (Fig. 1). Preheating of the gaseous fuel jet is attained by filling the fuel delivery cylinder with glass beads supported on a recessed metal screen, and surrounding the unit with a cylindrical resistance heater. The temperature of the cylinder wall and of the glass beads is monitored by means of suitably located thermocouples.

A typical experiment consists of measuring over a range of mass fluxes of gaseous fuel m_G the steady-state mass flux of solid propellant m_S necessary to feed the diffusion flame. Preceding ignition, the distance between the outlet of the fuel jet and the solid-propellant surface is carefully adjusted with the aid of a cathetometer and maintained constant during the experiment. The appearance of the diffusion flame is shown in Figure 2. The solid has assumed a slightly convex surface, a condition that obtains at high values of m_G but does not seem to affect m_G materially. The striations seen in the photograph result from the particulate combustion products of the CC passing through the diffusion flame. Their luminous streaks are indicative of the flow pattern prevailing near the flame. In this system the condition of maximum reaction rate is attained when m_S reaches a maximum value and becomes independent of m_G .

The solid strands were prepared from crystalline AP (reagent grade, manufactured by Matheson, Coleman and Bell) which was oven-dried at 120°C, ball-milled in a porcelain container, and subsequently sieved into size-graded fractions on stainless steel sieves. The particle size of AP employed in our study was limited to the range from 61-89 microns.

The catalyst CC (copper chromite Cu O202p, manufactured by Harshaw Chemical Co.) was added to the AP in the proportions needed to yield 3 and 5 wt%. The powdered mixture was pressed into 0.6-cm diameter strands at 10,000 psi.

Experimental Results

The parameters studied by means of the HOFD included (1) the composition of the solid oxidizer phase (concentration of CC), (2) the concentration of methane in the fuel gas, (3) the temperature of the fuel gas. In addition, an attempt was made to study experimentally some of the fluid-dynamic effects associated with variations in distance between fuel jet and oxidizer surface and the diameter ratio of fuel jet and propellant strand.

In a series of measurements it was observed that a distance of 6.5 mm between fuel gas outlet and solid propellant surface resulted in a flame of high stability and nearly cylindrical shape (when the solid began to form a conical surface, the flame would tend to conform to this shape). Also, when the diameter of the fuel jet exceeded by a factor of four that of the propellant, the propellant mass flux for a given fuel gas velocity remained constant and independent of jet size. The following results were obtained with fuel jets issuing from a cylindrical delivery tube with a diameter of 25 mm and a propellant strand diameter of 6 mm.

The results presented in Figure 3 show the effects of catalyst loading on the variation of propellant mass flux with fuel velocity. Of special interest is the critical mass flux m_s^* corresponding to the limiting rate of propellant consumption with increasing fuel mass flow. It is to be noted that, at a given methane mole fraction in the fuel stream, the value of m_s^* increases significantly as the catalyst concentration in the solid phase is increased from zero to five wt%. The

effect of initial gas temperature on the mass flux of propellant is demonstrated in Figure 4 for a system containing AP/CC (3 wt%) in the solid phase and 25 vol% methane in the gas jet. Although the relative increase in the value of m_S^* amounts to about 20% as the gas temperature is increased from 300 to 523°K, the general appearance of the curve is altered appreciably at the higher gas temperature. The relatively rapid attainment of the maximum in m_S observed at 300°K is spread out at the higher temperature. Physically this effect manifests itself in a more stable diffusion flame which tends to move in the radial direction at higher fuel gas temperature as m_G is increased.

Discussion

The general behavior of the HOFD exhibits some of the characteristics indicated by the mathematical model.⁸ Specifically, it allows an interpretation of the experimental result in terms of reaction-rate parameters. Considering the variation of m_S as a function of m_G , one can deduce that value of the fuel mass flux at which the oxidizer mass flux approaches a limiting value. As shown by the first three entries in Table 1, the ratio of these limiting mass fluxes corrected for the mole/fraction of fuel ($m_S^*/m_G^* \cdot N_G$) appears to be nearly constant. It suggests that the kinetics occurring in the diffusion flame are of first order in the methane concentration. Thus we may estimate the value of m_S^* at 100 vol% CH₄, recognizing the fact that m_G^* exhibits little change with methane concentration. On this basis a value of m_S^* of 0.2 g·cm⁻²sec⁻¹ is computed for AP/3CC/100CH₄, corresponding to a linear regression rate of 0.1 cm sec⁻¹. Similarly a comparison of the values of $m_S^*/m_G^* \cdot N_G$ as a function of the CC concentration in the condensed phase (Table 1) exhibits a linear dependence over the range of catalyst levels employed (Fig. 5). Thus for the system AP/5CC/100CH₄, the mass flux limit is found to be 0.3 g cm⁻² sec⁻¹ or a linear regression rate

of $0.15 \text{ cm} \cdot \text{sec}^{-1}$. These values are of the same magnitude as quoted in Reference 5.

Finally the HOFD results may be employed to estimate the overall activation energy of the combustion process for the system AP/CC/CH₄, in accordance with the theoretical development presented in Reference 8. To a first approximation for values of m^* ($m^* = m_S^*/m_G^*$) close to unity, the activation energy E is given by:

$$E \approx LR/[C_G (1-m^{*2})] \quad (1)$$

where L is the net heat of sublimation, given by the heat of sublimation of AP (500 cal/g) less the exothermic heat due to catalyzed solid phase reaction⁹ (370 cal/g), R the gas constant, and C_G the average specific heat of the gas. From the experimental data (Table 1) obtained at elevated gas temperatures (523°K), one calculates with $L = 130 \text{ cal/g}$, $C_G = 0.25 \text{ cal/g deg}$, and $m^* = 0.975$ a value of $E = 20 \text{ kcal/mole}$.

These results provide a quantitative input into current theoretical analyses of solid propellant combustion.¹⁰ As additional kinetic information is obtained with the aid of the HOFD on the rate processes involved in the heterogeneous combustion process, one will be able to assess the contribution of the kinetic and diffusional mass transport parameters for different propellant configurations and operating conditions. The dependence of the regression rate on both the properties of the solid (concentration of CC-catalyst) and the composition of the gas phase (methane concentration) as observed in our experiments points to some additional complexity in the quantitative description of the solid propellant combustion process.

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Table 1

LIMITING MASS FLUX DATA
FOR THE SYSTEM: AP/CC/CH₄

Solid (wt%)		Gas (vol%)		Temp	Limiting Mass Flux (g·cm ⁻² ·sec ⁻¹) × 10 ²			
AP	CC	CH ₄	N ₂	(°K)	m _S [*]	m _G [*]	m _S [*] /m _G [*]	m _S [*] /m _G ^{N_G}
95	5	49	51	300	12.6	1.3	9.7	20
97	3	49	51	300	10.4	1.3	8.3	17
97	3	24	76	300	7.2	1.8	4.0	17
100	0	24	76	300	5.0	1.7	2.9	12
97	3	24	76	523	8.8	9.0	0.975	4.1

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5. Effect of Catalyst Concentration on Mass Flux Ratio (Catalyst: Copper Chromite).

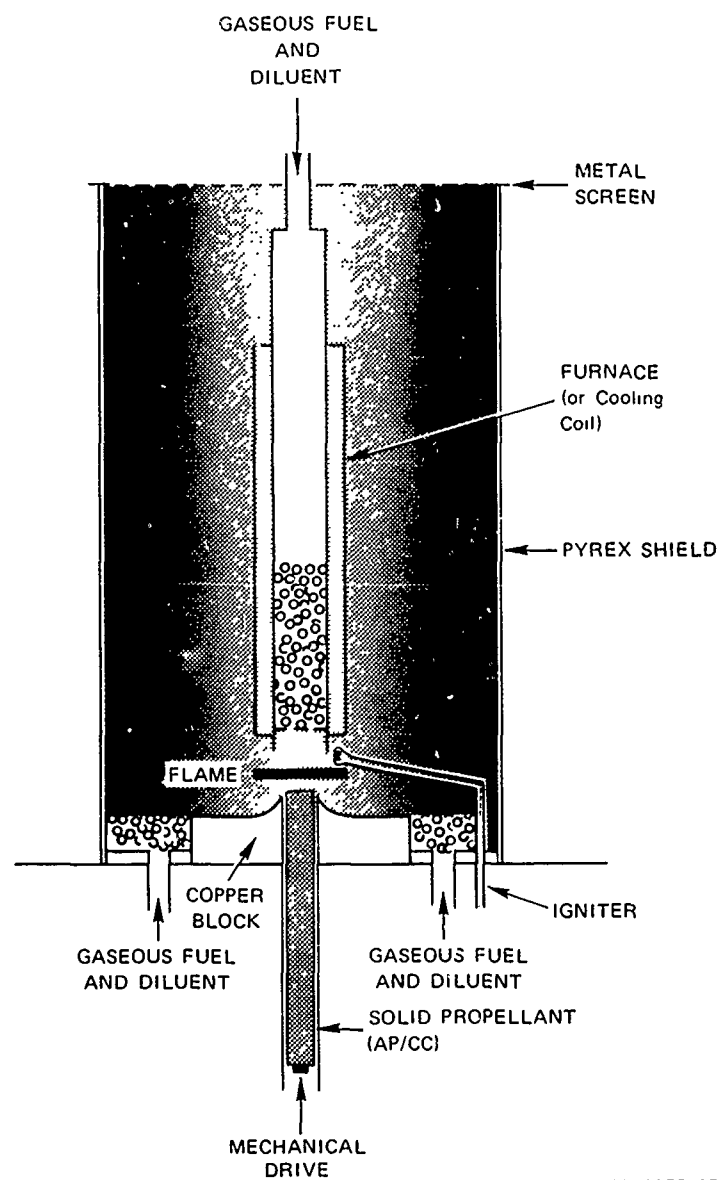


FIGURE 1 APPARATUS FOR HETEROGENEOUS OPPOSED FLOW DIFFUSION FLAME

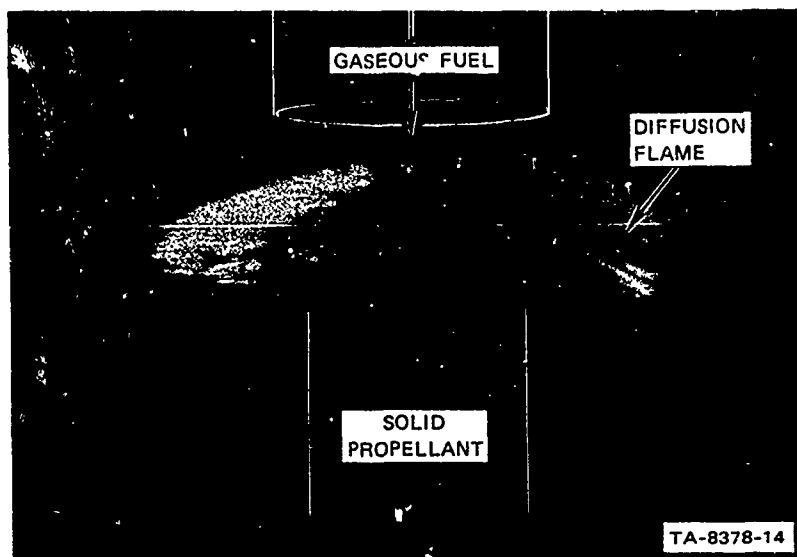
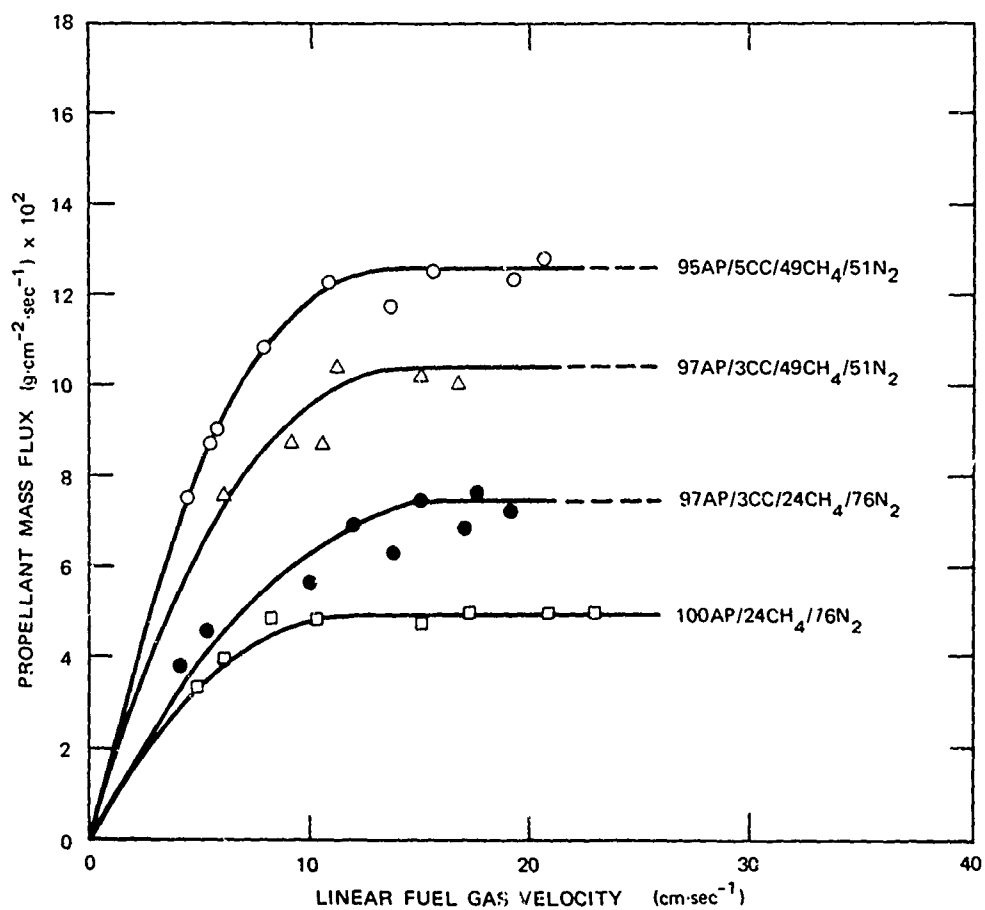
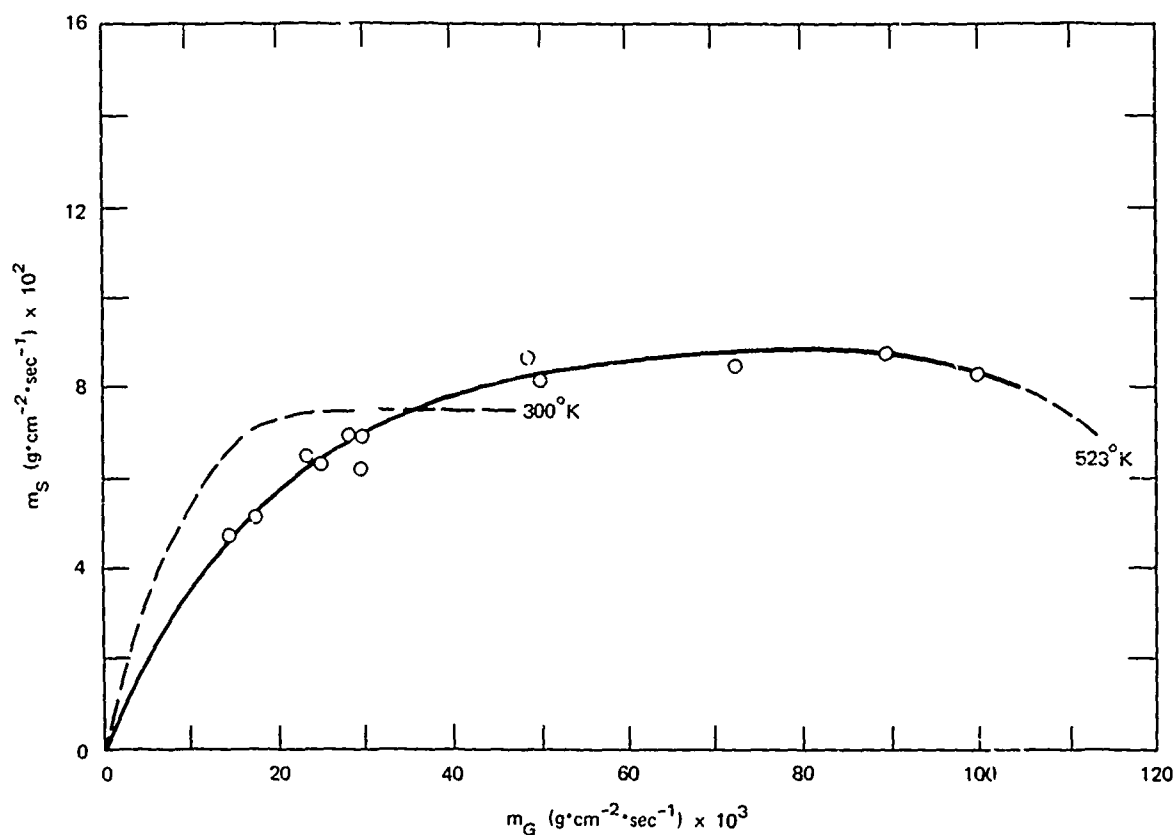


FIGURE 2 HETEROGENEOUS OPPOSED FLOW DIFFUSION FLAME
(Solid Propellant: AP/3CC; Fuel: CH_4 [24% vol.])



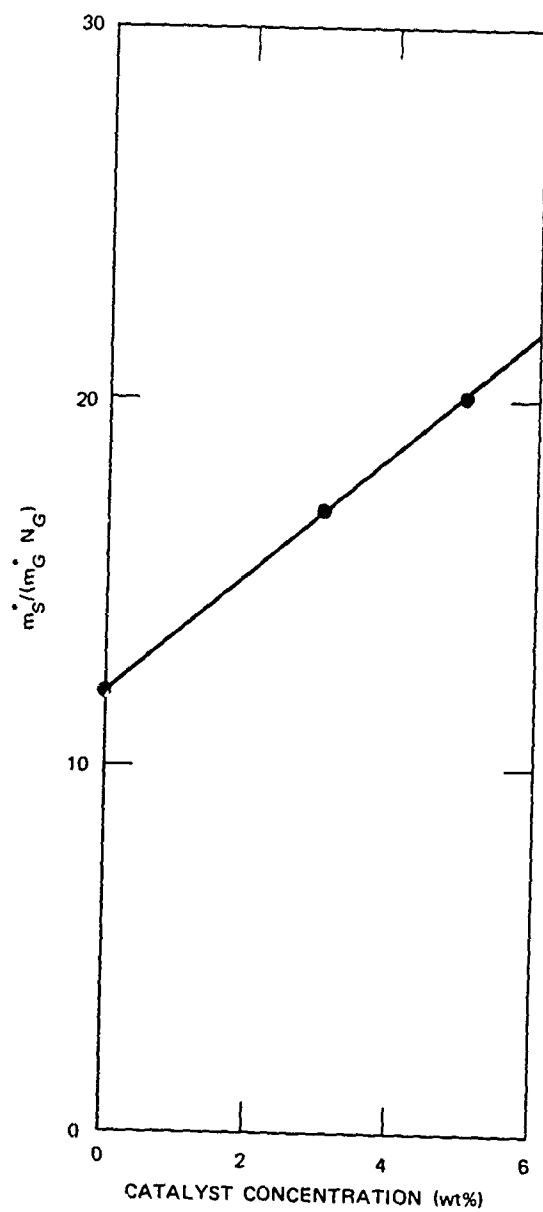
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FIGURE 3 VARIATION IN PROPELLANT MASS FLUX WITH GASEOUS FUEL VELOCITY



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FIGURE 4 PROPELLANT MASS FLUX AS A FUNCTION OF GASEOUS FUEL MASS FLUX AT DIFFERENT TEMPERATURES



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FIGURE 5 EFFECT OF CATALYST CONCENTRATION ON LIMITING MASS FLUX RATIO (Catalyst: Copper Chromite)